J. Serb. Chem. Soc. 67(10)669–676(2002)
JSCS-2989

UDC 546.72+543.48:556
Original scientific paper

Spectrophotometric determination of trace iron(III) in natural water after its preconcentration with a chelating resin

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(Received 2 February, revised 17 May 2002)

Abstract: A method for the determination of Fe(III) at trace levels is described. Thus, prior to the spectrophotometric determination, a preconcentration of the trace amounts of iron(III) using a chelate forming resin is proposed. A strong base anion-exchange resin (Dowex 2X4) loaded with Ferron (7-iodo-8-hydroxyquinoline-5-sulphonic acid) was used for Fe(III) preconcentration, at pH 2.2. After desorption with 5 % ascorbic acid in 0.5 M HCl, the analyte (converted from Fe(III) to Fe(II) was determined spectrophotometrically at 510 nm as Fe(II)-*o*-phenanthroline complex. The accuracy of the proposed method was verified by comparing the obtained results with those obtained using AAS with the standard addition method. The sensitivity of the spectrophotometric method (after preconcentration) was 0.01 μg Fe(III)/ml. The recovery for iron(III) at the 7 μg/l level was 97 %.

Keywords: iron(III), Ferron, chelating resin, preconcentration, spectrophotometric determination.

INTRODUCTION

Separation and preconcentration techniques are of great importance owing to the limited sensitivity of modern instrumental methods for trace analysis. Over the past ten years a large amount of data has been accumulated on chelating sorbents.[1–6] Among them, sorbents obtained by immobilization of chelating agents on solid supports have gained much attention.[1,6] High preconcentration factors obtained with the aid of these sorbents make them very useful in the analysis of environmental samples, particularly natural waters.[7–9]

The direct determination of trace iron from natural waters is limited and difficult when its concentration is too low to be determined directly and/or interferences due to the marix cannot be eliminated. For this reason, a series of papers[10,11] have reported the preconcentration of iron by using chelate-forming sorbents. Very efficient systems are provided by immobilization of 8-hydroxyquinoline on solid supports.[12–14] Also, a sulphonic acid derivative of 8-hydroxyquinoline, namely Ferron, (7-iodo-8-hydroxyquinoline-5-sulphonic

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acid), has been loaded on an anion exchange resin.[15] The obtained sorbent has been applied to the selective and quantitative separation of some metal ions from aqueous solutions, in the pH range 3 – 4.1. It was found that, in this pH range, the Ferron-loaded resin had a low affinity for Fe(III). But Ferron is one of the most selective chelating agents used in the spectrophotometric determination of Fe(III), at pH 2.6.[16]

In this connection, the conditions for Fe(III) sorption on a Ferron-loaded resin were examined. It was found that at pH 2.2, (adjusted with a buffer solution HCl–KCl), the sorption capacity of the chelating resin for iron(III) was optimum (0.55 mg/g resin). In a recent paper,[18] the efficiency of the Ferron-resin for sorption of Fe(III) at trace levels was demonstrated. A preconcentration factor of 80 was obtained.

As part of the cited investigations concerning the complexing properties of Ferron-resin towards Fe(III), this work was devoted to the spectrophotometric determination of trace iron after its preconcentratoin. Thus, after retention on the complexing resin at pH 2.2, the analyte is desorbed with ascorbic acid, (thereby being converted from Fe(III) to Fe(II)) and determined spectrophotometrically as the Fe(II)-*o*-phenanthroline complex, at 510 nm.

EXPERIMENTAL

Reagents

All solutilons were prepared with distilled water and all chemicals were of analytical-reagent grade.

The chloride form of a commercially available strongly basic anion exchange resin Dowex 2X4 (Dow, Germany), having dimethylethanolamine groups as the active fixed groups and a bead size of 100–200 mesh was used for preparing the chelating agent-loaded resin. The exchange capacity of the Dowex 2X4 resin was determined by converting a known amount of resin to the chloride form with an excess of 4 M HCl solution. After washing the resin thoroughly with distilled water, the chloride ions were eluted with 1 M $NaNO_3$ solution and determined by titration with a standard silver nitrate solution. The exchange capacity for anions was 3.98 meq/dry resin, in agreement with that declared.

Ferron, (7-iodo-8-hydroxyquinoline-5-sulphonic acid), produced by Merck, Germany, was used as the chelating reagent for the preparation of the complexing resin.

A 0.01 M iron(III) solution was prepared from ammonium iron(III) sulphate dodecahydrate in 0.01 M hydrochloric acid and standardized by reduction with tin(II) and then titration with a standard solution of dichromate. Solutions of lower concentrations were prepared by dilution of this stock solution just before use.

Aqueous metal ion solutions of Ca(II), Mg(II), Al(III), Mn(II), Co(II), Zn(II), Cr(III), Ni(II), Cu(II), Pb(II) were prepared by dilution of Titrisol standard metal salt solutions (Merck, Germany). Working solutions were freshly prepared from the standard metal salt solutions by dilution with distilled water.

Buffer solutions were prepared by usin 0.2 M HCl – 0.2 M KCl (pH 2.2) and 0.2 M ammonium acetate–0.2 M acetic acid (pH 3.5) in suitable ratios.

Solutions of ascorbic acid and hydroxylamine hydrochloride of different concentrations (2.5 % and 5 %) and in different acidic media (in presence of 0.1 to 1 M HCl), were tested as stripping agents for iron desorption from the chelating resin.

A 0.5 % *o*-phenanthroline solution was prepared in ethanol.

Apparatus

A Jasco V-530 double beam spectrophotometer equipped with a pair of 1 cm path length quartz cuvettes was used for the absorbance measurements.

An atomic emission spectrometer (ICP-AES, Varian, Liberty Series II, Australia) was used for the estimation of the composition of the natural water sample. The plasma was run at 700 V with 15 l/min argon. The operating conditions were the following: photomultiplier tube voltage, 700 V; incident power, 1.1 kW; plasma

gas flow, 15.01/min; auxiliary gas flow, 1.5 l/min; observation height, 14.0 mm; pump rate, 15.0 rpm; sample uptake time, 25 s; wavelength of elements (nm): Al, 308.215; Co, 228.610; Cu, 324.754; Mn, 257.610; Ni, 221.647; Pb, 220.383; Zn, 213.856. Ca(II) and Mg(II) were determined by the AAS technique.

A Pye Unicam atomic absorption spectrophotometer, AAS, Model SP 192, equipped with an air- acetylene flame burner and deuterium continuum source background corrector was used for the determination of all metal ions, before and after their treatment with the chelating resin. The absorption measurements of iron were performed under the following conditions: wavelength, 248.3 nm; window slit, 0.2 mm; current, 6 mA; acetylene flow, 1.1 l/min; air flow, 1 l/min; observation height, 10 mm.

The pH adjustment of buffer solutions was made using a Labor pH-Meesgerät, Model MV 84 pH meter, equipped with a glass electrode and a saturated calomel electrode with 0.1 M KNO_3 salt bridge, as the standard reference electrode.

Procedure

Preparation of the chelate forming resin. The batch method was used for the retention of Ferron on the resin. Thus, a weighed amount (0.2 g) of dry resin in the Cl^- form and 10 ml of a 5×10^{-3} M Ferron solution diluted to 20 ml with distilled water were mixed until the supernatant solution became colourless. Then, the loaded resin bed was filtered off on a fritted-glass funnel and washed with distilled water.

Metal sorption procedure. Weighed amounts (0.2 g) of chelating resin (loaded with 50 μmol of Ferron) were equilibrated with aliquots (10 ml) of buffer solution (pH 2.2) by shaking the mixtures with a mechanical shaker for 30 min. Aliquots (1 ml) of solutions containing 50 μg metal ion per ml were added to each vessel fitted with a glass stopper and the mixtures were shaken for 2 h. Each supernatant solution was separated by filtration on porous glass, washed with the buffer solution. The supernatant and washing buffer were collected in a 25-ml volumetric flask. The amount of sorbed metal ions was estimated by difference from the total amount added, using the AAS technique.

Procedure for the desorption of Fe(III) from the Ferron-resin. Samples of complexing resin to sorb the Fe(III) were stirred with 10 ml of a reagent solution to be tested as a stripping agent. Each mixture of stripping agent and resin was stirred for a definite shaking time (for 5 min to 1 h). The resin was then separated by centrifuging and iron was washed-out by means of a small volume of distilled water. The supernatant solution and the rinsing water were collected in a 25 ml volumetric flask. The amount of iron in the filtrate was determined by the AAS technique.

Measurement of Fe(II) – o-phenanthroline complex by spectrophotometry. Aliquots of standard solutions containing suitable amounts of Fe(III) were placed into 25 ml calibrated flasks. Then, volumes of 10 ml of 5 % ascorbic acid in 0.5 M HCl were added. After allowing the mixtures to stand for 10 min, the following reagents were added: 1 – 2 ml of 2 M NaOH; 7 ml of acetate buffer solution, to adjust the pH to 3.5 and 1 ml of 0.5 % *o*-phenanthroline. Then, the flasks were diluted to the mark with distilled water and mixed. A waiting time of 5 min was selected as sufficient for the generation of the Fe(II)-*o*-phenanthroline complex. The absorbances of these solutions were measured at 510 nm, *vs*. a reagent blank containing all reagents except the metal ion. A calibration graph of absorbance *versus* concentration was constructed.

Procedure for determination of iron after its preconcentration. A weighed amount (0.5 g) of Ferron-modified resin (loaded with 50 μmol Ferron) was stirred with a 150 ml aliquot of Fe(III) solution at a concentratoin of 0.01 μg/ml and having a pH of 2.2 (adjusted with HCl–KCl buffer). After equilibration for 2 h on a mechanical shaker, the supernatant solution was separated from the resin by filtration through a fritted-glass funnel and washed with distilled water. Subsequently, the resin was treated with 10 ml of 5 % ascorbic acid in 0.5 M HCl and the mixture was shaken for 30 min to desorb the iron as iron(II). The acid solution containing the desorbed iron was collected in a 25 ml volumetric flask and the general procedure for the spectrophotometric determination of iron applied. Then, the resin was treated successively with two and three 150 ml aliquots of iron(III) solution (0.01 μg/ml). After the last portion of the supernatant solution had been eliminated, the metal ion was recovered and determined in a manner similar to that described above.

RESULTS AND DISCUSSION

Sorption of metal ions

As was found in a recent study,[17] Fe(III) is quantitatively sorbed on the Ferron-loaded resin at pH 2.2 (adjusted with HCl–KCl buffer). In a continuation of the cited paper, the behaviour of other metal ions toward the chelating resin were studied under the same conditions. The results given in Table I show that Ca(II), Mg(II), Zn(II), Cr(III) are not retained while a small retention of Al(III), Mn(II), Co(II) and Pb(II) was observed. Also, the reslts indicated that at pH 2.2 the Ferron-resin has significant affinities for Cu(II) and Ni(II). This behaviour indicates the similarity between the retention of these metal ions in the complexing resin and the stability of the metal ions-ligand complexes in solution. Preliminary experiments showed that these complexes have low stability in solution, at pH 2.2 (their absorbances were small or insignificant except for the Cu(II)-Ferron and Ni(II)-Ferron complexes).

TABLE I. Results of desorption of some metal ions from the complexing resin, in the presence of 10 ml 5 % ascorbic acid in 0.5 M HCl

Metal ion[a]	Amount of metal ion fixed in resin[b]/μmol	Amount of metal ion after shaking with the stripping agent[b]/μmol	
		In resin	In solution
Al(III)	1.12±0.02	<1.12±0.01	<0.01±0.01
Mn(II)	4.41±0.01	4.35±0.02	0.06±0.01
Co(II)	2.00±0.03	1.99±0.02	0.01±0.01
Ni(II)	13.68±0.03	8.56±0.03	5.12±0.02
Cu(II)	49.25±0.05	41.44±0.05	7.81±0.03
Pb(II)	2.61±0.03	0.75±0.03	1.86±0.02

[a]Amount of metal ion in sample: 50 μg; [b]Data are the average of three determinations

Inlfluence of the stripping agent type on iron desorption

The effect of the stripping agent on the desorption of iron(III) from Ferron-loaded resin was investigated. The influence of the acidic medium was studied using different hydrochloric acid concentrations for reagent solutions containing 2.5 % or 5 % ascorbic acid or hydroxylamine hydrochloride. The results of these experiments are presented in Table II, from which is can be seen that Fe(III) cannot be desorbed quantitatively by using only 0.1–1 M HCl. This proves that the Fe(III)–Ferron complex, formed in the resin, is stable in presence of the mentioned reagents. For this reason two reductive agents were tested as stripping agents, namely ascorbic acid and hydroxylamine hydrochloride, in different acid media. As shown in Table II, Fe(III) can be desorbed quantitatively as its reduced form by using 5 % ascorbic acid in 0.5 or 1 M HCl. So, this stripping agent destroys the Fe(III)–Ferron complex. The resulting Fe(II) does not form a complex with Ferron. Hence the metal ion is desorbed from the complexing resin.

TABLE II. Desorption behaviour of iron from the complexing resin in presence of various stripping agents

Stripping agent	Acidic medium	Recovery[a]/%
2.5 % Ascorbic acid	HCl 0.1 M	57±0.5
	HCl 0.5 M	75±1.0
	HCl 1 M	78±0.8
5 % Ascorbic acid	HCl 0.1 M	60±1.0
	HCl 0.5 M	100±0.5
	HCl 1 M	100±0.6
2.5 % Hydroxylamine hydrochloride	HCl 0.1 M	30±1.1
	HCl 0.5 M	65±1.5
	HCl 1 M	73±1.0
5 % Hydroxylamine hydrochloride	HCl 0.1 M	42±1.0
	HCl 0.5 M	77±0.5
	HCl 1 M	85±0.7
HCl	0.1 M	18±1.0
	0.5 M	58±0.5
	1 M	65±0.7

[a]Data are the average of three determinations. Amount of Fe(III) fixed in the resin: 50 μg; amount of resin: 0.2 g (loaded with 50 μmol Ferron); volume of stripping agent: 10 ml; shaking time: 1 h

Effect of shaking time on iron desorption

As a result of the previous experiments, 5 % ascorbic acid in 0.5 M HCl was selected as the stripping agent for iron desorption. Experiments showed that the desorption of iron was quantitative after a shaking time of 30 min.

Desorption of metal ions from the loaded resin

The elution behaviour of the other metal ions in presence of 5 % ascorbic acid in 0.5 M HCl are presented in Table I. It was assumed that the metal ions-ligand complexes in the resin were not affected by the presence of ascorbic acid as reductive reagent. It was assumed that the hydrochloric acid in the stripping agent is responsible for the small recoveries of some metal ions.

Spectrophotometric determination of Fe(II) as its o-phenanthroline complex

Based on the optimum conditions described above, Fe(III) can be desorbed quantitatively from the complexing resin just in its reduced form Fe(II), which could be determined spectrophotometrically. For example, *o*-phenanthroline is one of the more selective chelating agents used for the spectrophotometric determination of Fe(II).[19] It was found that the lower limit for the quantitative determination of Fe(II) is 0.1 μg/ml (when using 1 cm path length quartz cuvettes).[19] This result was obtained by working in presence of hy-

droxylamine hydrochloride as the reductive agent. We obtained similar results by working ini presence of 5 % ascorbic acid in 0.5 M HCl. Hence, the general procedure for the measurement of metal ion -*o*-phenanthroline complex by spectrophotometry was applied.

It was found that Beer's law is obeyed over the concentration range from 0.1 to 5 μg Fe(III)/ml, with a correlation coefficient of 0.997.

Spectrophotometric determination of trace iron after its preconcentration

The experiments were carried out following the described procedure for the determination of Fe(III) after its preconcentraton. After the first test of preconcentration, Fe(III) was preconcentrated by a factor of 15. The data in Table III show that this first test of concentration was not sufficient to determine Fe(II) spectrophotometrically.

TABLE III. Reslts of the spectrophometric determination of iron(III) after its preconcentration on the Ferron-resin

Test No.	Sample volume/ml		Concentration of iron[a]/(μg/ml)		
	Initial	Final	Before preconcentration	After preconcentration	
			Calculated	Calculated	Determined[c]
1	1[b]×150	25	0.01	0.060	–
2	2[b]×150	25	0.01	0.120	0.115±0.001
3	3[b]×150	25	0.01	0.180	0.178 ± 0.002

[a]Data are the average value of three determinations. [b]1–3 represents the number of 150 ml aliquots of the water sample containing Fe(III) added successively to the Ferron - loaded resin. [c]Amount of loaded resin: 0.5 g; amount of Ferron in resin; 50 μmol

The second and third tests of preconcentration resulted in an iron preconcentration of 30 and 45 fold, respectively. The data in Table III indicates that these preconcentration experiments allowed an improvement of the senstivity in the determination of iron.

From the experimental results it is clear that for the spectrophotometric determination of iron in dilute solution, it is necessary for the solution to be preconcentrated so that the amount of metal ion retained in the resin and then eluted with a minimum volume of stripping agent (in this experiment 10 ml of 5 % ascorbic acid in 0.5 M HCl), is enough to reach the lower limit for quantitative determination of iron by the proposed spectrophotometric method.

So, before preconcentration, the concentration of metal ion (0.01 μg/ml) was below the sensitivity of the spectrophotometric method (0.1 μg/ml). Hence the error of the spectrophotometric determination of iron. When the complexing resin was stirred successively with two and three respectively 150 ml aliquots of 0.01 μg/ml solution, the total amount of iron retained in the chelating sorbent and then released with 10 ml of 5 % ascorbic acid in 0.5 M HCl was enough to exceed the lower limit for quantitative determination of iron by the spectrophotometric method (0.1 μg/ml).

Sample analysis

The accuracy of the preconcentration method was investigated using a natural water. Its composition was determined by the ICP-AES technique (except Ca(II) and Mg(II), which were determined by AAS), under the mentioned working conditions (see "Experimental"). The reslts of the iron determination by AAS, after preconcentration were in good agreement with those obtained by AAS using the standard addition method (Table IV). Recovery at the 7 μg Fe(III)/l level was 97 %.

As mentioned before, Ca(II) and Mg(II) are not retained on the Ferron-resin. The other elements present in the natural water (Al(III), Ni(II), Mn(II), Cu(II)) which could be sorbed on the resin and then released by the stripping agent do not interfere, at this level of concentration, in the determination of iron by the proposed spectrophotometric method.

TABLE IV. Analysis of trace iron(III) in a natural water sample

Composition of water sample μg/ml[a]	Fe(III)[α]/(μg/l)	
	Without preconc.[b]	Proposed method[c]
Ca(II),46.09;Mg(II),13.37; Al(III),0.002;Ni(II),0.001; Mn(II),0.019,Zn(II),0.008; Co(II),0.001;Cu(II),0.001; Pb(II),0.001.	7.0±0.2	6.8±0.2

[a]The ICP-AES technique (Mg(II) and Ca(II) were determined by AAS); [b]The AAS technique was combined with the standard addition method. [c]Amount of loaded resin: 0.5 g; amount of Ferron in resin: 50 μmol, sample volume: 450 ml; eluent volume: 10 ml; stripping agent: 5 % ascorbic acid in 0.5 M HCl. [d]Data are the average of three determinations

CONCLUSION

The results presented in this paper indicate that the described method can be regarded as an alternative to the determination of Fe(III) by a more sensitive method. Thus, Fe(III) could be determined by AAS with a calibration curve or by the standard addition method from a solution with an iron(III) concentration under 0.1 μg/ml.

In this paper, an alternative method to AAS, namely the indirect determination of Fe(III) as trace levels by a spectrophotometric method, after its preconcentration with a Ferron-loaded resin, is presented. By applying this procedure to the analysis of a real sample, a recovery of 97 % (at the 7 μg/l level), was achieved.

The proposed method allows for an improvement in the sensitivity in the spectrophotometric determination of Fe(III) (after its preliminary reduction to Fe(II) as metal ion-*o*-phenanthroline complex), from 0.1 to 0.01 μg/ml.

ИЗВОД

СПЕКТРОСКОПСКО ОДРЕЂИВАЊЕ ТРАГОВА ГВОЖЂА(III) У ПРИРОДНИМ ВОДАМА ПОСЛЕ ЊЕГОВЕ ПРЕДКОНЦЕНТРАЦИЈЕ ХЕЛАТИРАЈУЋИМ СМОЛАМА

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Описана је метода одређивања Fe(III) у траговима. Пре спектроскопског одређивања количине Fe(III) у траговима су предконцентрисане коришћењем смола које формирају хелате са Fe(III). За предконцентрисање је коришћена јака базна анјон-измењивачка смола (Dovex 2X4) претходно обрађена са Фероном (7-јодо-8-хидрохинолин-5-сулфонска киселина) при pH раствора Fe(III) једнаком 2,2. После десорпције са раствором 5 % аскорбинске киселине у 0,5 M HCl концентрација јона гвожђа, после претходног превођења Fe(III) у облик Fe(II), одређивана је спектрофотометријски у облику Fe(II)-*о*-фенантролинском комплексу на 510 nm. Тачност предложене методе верификована је упоређењем са резултатима добијеним методом атомском апсорпционом спектроскопијом методом стандардног додатка. Осетљивост спектроскопске методе после предконцентрације била је 0,01 mg Fe(III)/ml. Ефикасност на нивоу од 7 μg/l била је 97 %.

(Примљено 2. фебруара, ревидирано 17. маја 2002)

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